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DETERMINATION OF FRYING MEDIUM QUALITY LIFE

A Thesis

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By

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ABSTRACT

DETERMINATION OF FRYING MEDIUM QUALITY LIFE

by Clay A. Glanz

Quick assay methods which are currently available were used to determine the quality life endpoint of a frying medium. French fries were fried for 21 days (12 hours/day). Samples of french fries and frying medium were taken every 2 hours. Sensory panels were conducted twice a day. Endpoints for the frying medium based on each assay method were then calculated and compared to the sensory endpoint of the french fries. The results indicated that the various assay methods, including %Polars, %Free Fatty Acids (%FFA), dielectric constant and color, all linearly increased with time. However, the assay methods indicated very different endpoints based on accepted food industry limits. The french fries lost sensory acceptance based on greasiness by day 15 of the study. The %FFA endpoint was 7 days, %polar materials kit was 17 days and the dielectric constant was 20 days.

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DEDICATION

This thesis is dedicated to my girlfriend, Leslie Grassi, and her cat Harold, whose support and comfort helped me through all the difficult times. Without their support, none of this would have been possible.

PREFACE

The following is a publication style thesis. The second chapter is written in journal format according to 1990 guidelines and will be submitted to the Journal of Foodservice Systems. Chapters I and III are written according to guidelines outlined in the Publication Manual of the American Psychological Association, 3rd. edition, 1986.

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CHAPTER 1

INTRODUCTION AND REVIEW OF LITERATURE

Introduction

Deep fat frying is one of the most commonly used procedures for preparation and manufacture of foods (Olieman, 1983; Chang et al., 1978). In deep fat frying the food is completely surrounded by the frying medium. The frying medium acts as a heat transfer medium. The higher temperatures possible with deep fat frying result in more rapid heat penetration, therefore making it a more efficient method than the dry heat of an oven or boiling in water (Stevenson et al., 1984).

Since the use of deep fat frying as a means of food preparation is so widespread in the foodservice industry, methods to effectively monitor the process of deep fat frying are essential. The results of this study will contribute to the available information on methods used to monitor the degradation of frying media in foodservice environments.

A variety of chemical and physical changes take place in both the food and the oil during frying. Some of these changes are beneficial in that they contribute to the sensory qualities of the food. However, extensive decomposition, resulting from inadequate control of the

frying process, can lead to decreased sensory acceptability and nutritional value, and the development of off flavors (Nawar, 1985). It is therefore economically important to maximize the shelf life/usage life of the frying oil.

According to Talley et al. (1987) the quality of deep fat fried foods is dependent upon the following:

1) Type and initial quality of the oil
2) Stability of the oil
3) Quality of the food being fried
4) Presence of pro-oxidants such as metals
5) Time and temperature of frying
6) Time and temperature of idling fry kettles
7) Surface area of fry kettles
8) Cleaning procedures for oil and kettles

While there is little debate relating these factors to the quality of fried foods, there is substantial debate regarding techniques to use to monitor the thermal degradation of the frying medium. Controversy exists regarding accuracy and the ability to monitor based on the relative stability of the degradation compound being measured. Methods used to monitor the degradation of frying media in foodservice testing environments should be inexpensive and uncomplicated based on the large number of samples being taken.

The methods employed should ideally measure compounds which develop as a result of frying media breakdown, but are not volatilized or affected by the type of food being fried. Since any instrumental method of analysis must ultimately correlate with the quality of the fried product, it is critical that the method also correlate with sensory analyses of fried foods cooked in the frying medium in question.

Objectives

The objectives of this study were:

1) to evaluate various quick assay methods for measuring thermal degradation in a commercial frying medium under realistic industry conditions;

2) to provide information on days of quality life as measured by the different assay methods based on published criteria;

3) to correlate the days of quality life for the frying medium as measured by the objective measurements with the upon sensory test results for french fries prepared in the frying medium;

4) to recommend a quick assay method for measuring the thermal degradation of frying media based on ease of use and correlation to sensory test results, and

5) to compare thermal degradation in two fryers with different fryer design.

Significance of the Study

Since the use of deep fat frying as a means of food preparation is so wide spread in the foodservice industry, methods to effectively monitor the process of deep fat frying are essential. There is still disagreement among researchers about the best techniques to monitor thermal degradation of frying media. It is essential to measure stable degradation products. It is unlikely that these products will be affected by the various conditions to which they are exposed to during heating and testing. The results of this study will contribute to the available information on methods used to monitor the degradation of frying media in foodservice environments.

Review of Literature

Chemistry of Thermal Degradation

Thermal Degradation

During the thermal degradation of frying oils (shortenings) the lipids involved become thermally oxidized to produce a number of decomposition products (Nawar, 1985). Oils deteriorate more or less slowly depending on the amount of heating and type and amount of food fried.

The degradation of frying media occurs in stages (Weiss, 1983). A brief induction period is followed by the formation of peroxide radicals which quickly degrade to hydroperoxides and then to other decomposition products. The level of oxygen in the oil continues to rise as the peroxide levels decrease. Further breakdown products accumulate as polymerization and viscosity increase in the oil. Oil degradation can be slowed down by the introduction of foods which can in essence absorb and strip off, in the form of steam, some of the degradation compounds. However, it is important to remember that foods can also accelerate oil degradation by introducing soluble chemicals into the oil. In addition, new oil is frequently added to fryers during use which can also slow down degradation by dilution effect. This dilution effect, or turnover rate (Weiss, 1983) is probably the most important factor in retaining frying fats in satisfactory condition. The added fat should amount to 15 - 25% of the capacity of the kettle/fryer (Weiss, 1983).

There are numerous degradation products formed during the thermal degradation process. These products include a series of aldehydes, ketones, acid esters, alcohols, hydrocarbons, lactones, cyclic compounds, dimers and polymers. The relative amounts of these compounds can vary

widely depending on the nature of the substrates and the parameters of the heat treatment.

The primary reaction pathways involve the formation and the decomposition of hydroperoxide intermediates with similar qualitative patterns (Frankel, 1979). The formation and destruction of these hydroperoxides is extremely rapid at high temperatures as are the resulting primary decomposition products which undergo further oxidative decomposition. As the oxidative process continues, a number of reaction mechanisms can occur which result in the development of hundreds of compounds (Chang & Paulose, 1973; Chang et al., 1978; Frankel, 1982; Selke et al., 1975a, 1975b; Nawar et al., 1977).

Degradation Products

There are numerous degradation products formed during this process. These products include a series of aldehydes, ketones, acid esters, alcohols, hydrocarbons, lactones, cyclic compounds, dimers and polymers. The relative amounts of these compounds can vary widely depending on the nature of the substrates and the parameters of the heat treatment.

The primary reaction pathways involve the formation and decomposition of hydroperoxide intermediates with similar qualitative patterns (Frankel, 1979). Experimental evidence indicates that hydroperoxides are the predominant, but not

exclusive, intermediate products of oxidation of unsaturated fats (Nawar, 1985; Weiss, 1983). Hydroperoxides are relatively unstable at or above 80 C, whereas at room temperature they are relatively stable. Therefore, different end products may be produced under different reaction temperatures. The polyethenoic acids (linoleic, linolenic, arachidonic, etc...) are more readily oxidized than the monoethenoic acids (oleic, palmitoleic, etc...).

Hydroperoxide Formation and Decomposition

Hydroperoxides. A mechanism for the oxidation of a methylene interrupted unsaturated system (e.g. linoleate) was proposed by Holman (1954). The proposed mechanism involves three stages of reactions: initiation of the chain reaction, chain propagation, and chain termination. In the initiation step, a hydrogen atom is removed from the methylene carbon atom adjacent to the double bond. This reaction results in the formation of a free radical. The reaction can be catalyzed by trace metals, pigments such as chlorophyll, light, or enzymes such as lipoxigenases. Without these catalysts, the reaction would be too slow to be significant. The free radical is a resonance hybrid. Molecular oxygen adds to the resonating radical, primarily at the ends, to yield two types of hydroperoxy radicals. These free radicals can accept hydrogen atoms from other

molecules (linoleate) to become isomeric conjugate cis, trans - hydroperoxides and in doing so propagate the chain reaction. Theoretically only a single molecule needs to be involved in order to propagate the chain reaction of autoxidation. The reaction can be terminated by the collision of radicals with each other as follows:

$$ROO^* + R^* \rightarrow ROOR$$

$$R^* + R^* \rightarrow RR$$

$$ROO^* + ROO^* \rightarrow ROOR + O2$$

Decomposition of Hydroperoxides. The formation and destruction of these hydroperoxides is extremely rapid at high temperatures, as are the resulting primary decomposition products which undergo further oxidative decomposition. They enter into numerous and complex breakdown and interaction mechanisms responsible for the production of many compounds of various molecular weights. Each hydroperoxide produces a set of initial breakdown products that are typical of the specific hydroperoxide in question. An example of this is given for oleate and is shown in Figure 1 (Nawar, 1985). Hydrogen atoms are removed from oleate at carbons 8 and 11, resulting in the formation of two allylic radical intermediates. Oxygen attack at the end carbons of each radical produces an isomeric mixture of 8, 9, 10, and 11 allylic hydroperoxides. These

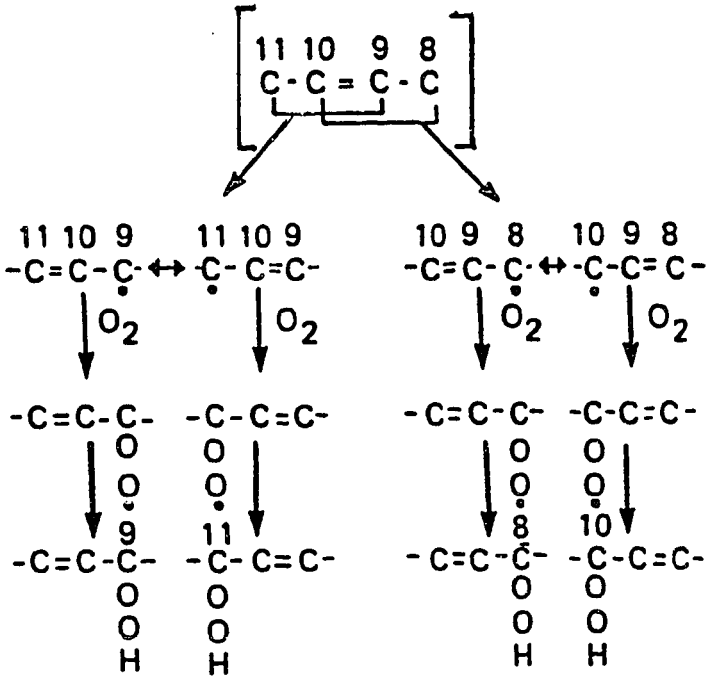

Figure 1. Formation of hydroperoxides.

hydroperoxides begin to decompose as soon as they are formed. The first step in hydroperoxide decomposition is cleavage at the oxygen-oxygen bond of the hydroperoxide group giving rise to an alkoxy radical and a hydroxy radical.

The second step in hydroperoxide decomposition is cleavage of the carbon-carbon bond on either side of the alkoxy group. Cleavage on the carboxyl side results in the formation of an aldehyde and an ester; cleavage on the methyl side produces a hydrocarbon and an oxoacid. Again referring to Nawar's (1985) example of oleate, cleavage on the hydrocarbon side of the 8-hydroperoxide isomer of oleate would produce decanal and methyl-8-oxooctanoate, and cleavage on the carboxyl side forms 2-undecenal and methyl heptanoate.

As expected, each remaining hydroperoxide of oleate would produce four typical products. For the nine hydroperoxide, nononal, methyl-9-oxononanoate, 2-decenal, and methyl octanoate would be produced. For the 10 hydroperoxide, octane, methyl-10-oxo-8-decanoate, nonanal, and methyl-9- oxononanoate would be produced. For the 11 hydroperoxide, Heptane, methyl-11-oxo-9-undecenoate, octanal, and methyl-10 -oxodecanoate would be produced (Chang & Paulose, 1973; Chang et al., 1978; Frankel, 1982;

Selke et al., 1975a, 1975b; Nawar et al., 1977).

Changes During Frying

Figure 2 shows the general chemical changes which occur in oils during deep fat frying. It is evident that the food aerates the oil providing oxygen which can then cause the oxidation of the oil to produce the hydroperoxides. The hydroperoxides then can undergo 1) fission to produce alcohols and aldehydes which degrade to acids and hydrocarbons which with heating form dimers and cyclic compounds, 2) dehydration to ketones or 3) can form free radicals which can form dimers, trimers, epoxides, alcohols or hydrocarbons.

It is also evident from Figure 2 that the food can contribute both colored compounds (fat soluble pigments) as well as lipids (food fats/oils) to the frying system. It is also important to remember that the frying operation is a dehydration process taking place at the food/frying medium interface. Steam is generated which can carry off degradation compounds (volatile compounds) already formed in the frying oil as smoke or can hydrolyze the frying oil into free fatty acids, di-glycerides, mono-glycerides and glycerol. Pai et al. (1979) showed that the presence of water during heating resulted in substantial hydrolysis of

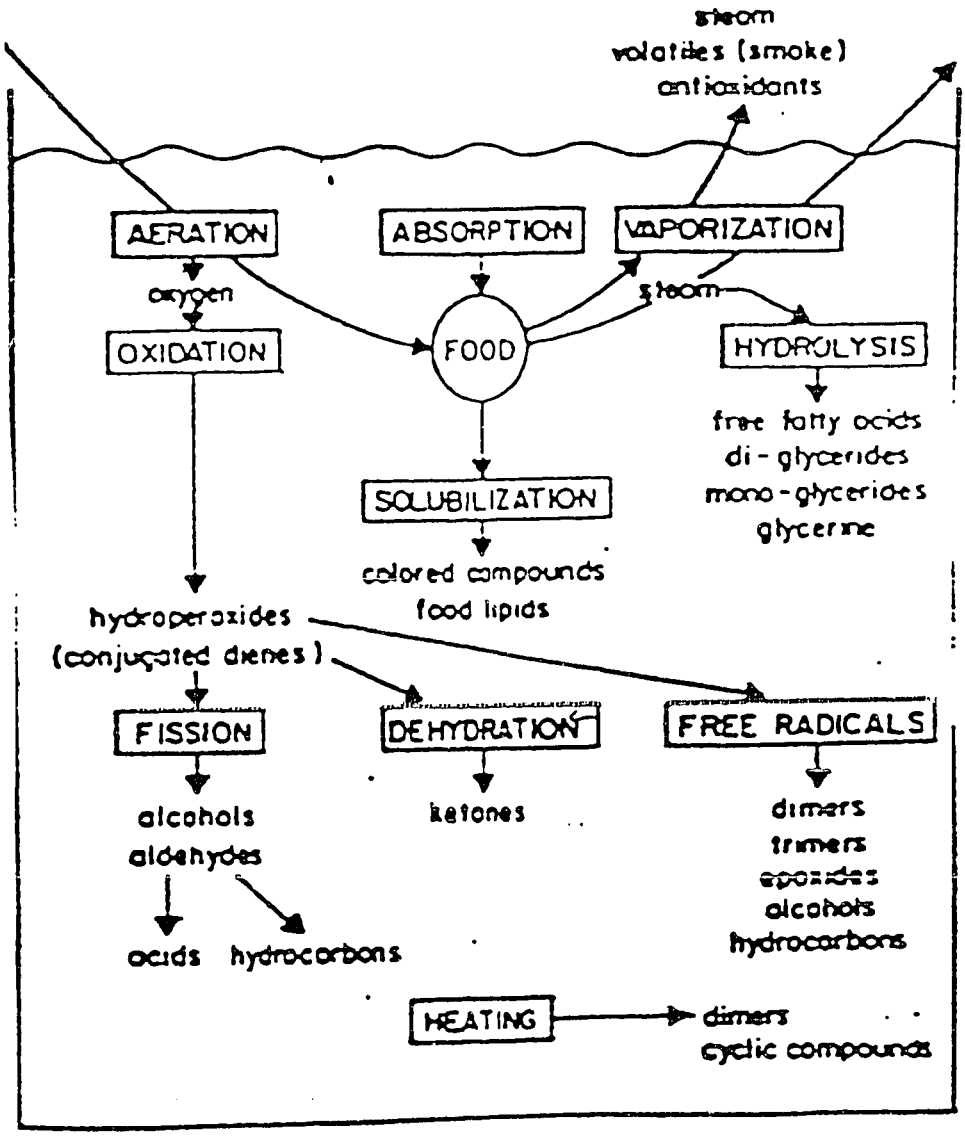

Figure 2. Changes occurring in frying media during deep fat frying.

the frying oil. This was seen as an increase in the amounts of C6 - C14 even numbered free fatty acids. The steam generated within the food being fried initially acts as a barrier to frying medium contact and conduction of heat to the food (Blumenthal,1987). As the frying medium continually degrades throughout the cooking process, the frying medium/water interface breaks down. Blumenthal (1987) stated that this effect was due primarily to increased levels of total alkaline materials which can act as surfactants in the frying medium. The consequence of this interface breakdown is that the temperature at the surface of the food increases due to closer proximity of the oil to the surface. The increased surface temperature in the product being fried results in the product becoming browner. This hypothesis accounts for the increased brown color noted for fried products as the frying medium undergoes thermal degradation. The hydrolysis of the triglycerides forms quantities of free fatty acids which can then react with oxygen to form other degradation compounds. These new compounds can be volatile in which case they are stripped from the frying oil by steam from the food. If they remain in the frying oil they can be soluble or can be colloidally suspended non-acid non-volatile products.

Methods Used to Measure Thermal Degradation

There are rapid analytical techniques to directly measure free fatty acids, oxidized fatty acids, carbonyls, polar materials and alkaline materials. There are also methods such as the Food Oil Sensor which measures thermal conductivity of the frying medium. The thermal conductivity of a frying medium changes due to alterations in chemical components which have been correlated to the development of degradation products. While there are other tests which monitor the formation of degradation products, such as polymers, the analytical techniques are long and involved.

The analysis method or methods which one chooses will be different based upon what one wishes to ascertain. The following are the basic criteria for selection of a method:

a - First, the rapid method(s) selected will depend on which degradation product(s) one wants to analyze. The degradation product(s) evaluated will depend on safety issues as well as other quality parameters.

b - Second, the rapid method chosen should be one which correlates well to standard analytical techniques for measuring the degradation products one has selected.

c - Third, the method should give consistent results from sample to sample and from operator to operator.

The following methods will be discussed based upon:

1 - the type of thermal degradation product which they measure.

2 - why the particular thermal degradation product is measured and how it is related to safety concerns or aesthetic quality of fried products.

3 - the principle of the rapid analytical technique and advantages of the technique.

4 - whether the rapid method is correlated to standard techniques for measuring thermal degradation.

5 - any special concerns or problems with the method.

Free Fatty Acids - The measurement of free fatty acids as an indicator of oil quality is a widespread practice because it is easy to do, and the percentage of free fatty acids does rise with increasing use of a single batch of frying oil (Smith et al., 1986; Talley et al., 1987). It should be noted that Smith et al., 1986 found the titration end point in the method difficult to determine especially with dark colored oils.

In contrast to the findings of these researchers, a number of other researchers have found the measurement of free fatty acids to be an unreliable indicator of oil quality (Fritsch, 1979; Mankel, 1970; Buxdorf et al., 1976; Croon et al., 1986; Blumenthal, 1987). These researchers

reported no direct relationship between free fatty acid levels and the quality of used frying oils. Wu and Nawar (1986) evaluated free fatty acid measurements along with eight other analytical techniques. While free fatty acids did increase with frying time, they were subject to dilution. Wu and Nawar (1986) did not find that free fatty acid values correlated to frying oil quality.

Blumenthal (1987) stated that the measurement of free fatty acids is nearly meaningless since many of the free fatty acids are continually being changed to volatiles and non-acidic, non-volatile decomposition products. The measured percent of free fatty acids is related to what is left over from other degradation processes. In addition, as was already mentioned, the free fatty acids can be diluted by the addition of new oil. The USDA regulation for free fatty acids is set at a maximum level of 2% in frying oil for fried products to be stored prior to use. It should be noted that oils that are used for frying foods which will be immediately consumed will still be high in quality at 3% free fatty acids. For establishments where the fried products will be immediately consumed, the endpoint for fried foods from a sensory standpoint can be 6% to 8% for trained and semi-trained panels and as high as 12% for untrained tasters (R. Stier, personal communication).

There are several methods to measure free fatty acids. The standard method for measuring %free fatty acids is the AOAC 28.029b or AOCS Ca5a-40 methods. While this is a lab technique, it is economical, and easily replicated. It does have the drawback that the titration endpoint can be difficult to see in very dark or degraded oils. The method does require a laboratory setting, standard lab equipment and training of personnel to perform the simple test.

A second method was developed by Robern and Gray (1981) and consists of a drop of oil being placed on a silica gel covered slide which has bromocresol-green incorporated in the gel. The gel then changes color in response to the pH change due to free fatty acids in the oil, with the color going from blue to green and then yellow as the fatty acids increase. The method required the manufacture of the slides and according to Croon et al. (1986) did not correlate well to changes in free fatty acids as measured by the standard method.

There is a third method patented by Jerry Milnar of 3M, St. Paul, MN in 1985, consisting of a test strip made from alpha-cellulose divided into separate regions by applying stripes of liquid silicone and then heat polymerizing so that the stripes became impenetrable barriers. Each cell had a non-volatile long chain polyhydric alcohol, various

levels of metal carbonate and an acid\base indicator dye. The cells in the strips were designed to indicate acid levels of 1 to 14 with 5 being the discard level for oils used for frying breaded foods and 9 the discard level for french fries. The method used non-toxic materials and according to the manufacturer had good correlation to free fatty acids. However, the strips are not discriminating enough at the level required by some users and do not correlate well to free fatty acids in this range (G. DeMenna, personal communication).

Another method used to measure %free fatty acids is the Veri-Fry FFA (Libra Laboratories) Diagnostic Quick Test. This is a test tube test which is based on the addition of the oil to be tested to a test tube containing an oil fraction gel and a pH sensitive indicator dye. The gel in the test tube is heated to 40C, the oil is added at 40C, and the free fatty acids are extracted with shaking from the oil into the gel. The color can then be compared to a color card which shows the relationship to titratable acidity. The test kits are inexpensive, require no special training to use and are rapid. The manufacturer has stated that they also are not subject to interference from dark degraded oil colors. Some care in handling the kits must be taken to assure that the temperature of the test tube remains at

least 40C. In addition, if you wish to quantify the readings by measuring spectrophotometrically, it is necessary to have a 1 mm cuvette.

Oxidized Fatty Acids - These are a component of the polar materials which are of concern from a health standpoint since high levels of polar materials could be potentially harmful (Billek et al., 1978). They can be measured using the Oxifrit Test (Merck & Co., Inc.). Formerly the Rau Test, this test kit monitors oxidized fatty acids in a test tube containing tertiary butyl alcohol as the primary solvent with the indicator dye, bromphenol blue. The test oil is dissolved in the solvent with the resulting color correlated to oxidized fatty acids. The method has good correlation to %polars measured by the standard technique and has good repeatability between labs. The method is used in Germany as an "endpoint" test (Blumenthal, 1987). However Blumenthal (1987) found that the method was sensitive to oil type and food color level. In addition to these problems, the kit contains a solvent system which is not GRAS, making it less desirable to use in institutional kitchen environments.

Color in Oil - The color of oil is not generally related to its ability to permit frying of light colored food. The colored compounds are inert with respect to the cooking

process (Blumenthal, 1987). Because color in oil can result from more than one chemical process, the use of color comparisons to judge oil quality is not valid when evaluating a wide range of frying situations.

The method recommended, AOCS Official Method Ca 13c-50, which has been updated as recently as 1981, is a photometric method. In this method the color of the oil is measured at several wavelengths. The absorbances at the various wavelengths are then introduced into an equation and an empirical color number derived.

Total Alkaline Materials - Alkaline materials are formed in frying oils during cooking. Alkaline materials are part of the polar material fraction of used oils. Alkaline materials include soaps and other highly surfactant materials. Blumenthal (1987) stated that a primary cause of decreased performance of a frying oil with use is often due to increased levels of alkaline materials. The interaction of food materials with the oil leads to increased alkalinity of the oil. These materials are also degradation products and can be related to the development of surfactants/soaps from the interaction of fatty acids with oxygen in the presence of trace amounts of metals. As surfactant levels increase in thermally degraded oils, oil penetration (pick-up) into fried products, especially breaded products, can be

expected to increase (Blumenthal et al., 1985).

In addition the color of the fried products can be expected to darken as heat and mass transfer conditions alter at the surface of the fried products. Essentially, as the surfactant levels increase, oil penetration overcomes the opposing pressure of water vapor at the food surface thereby allowing the food surface to heat up to higher temperatures with consequent increased surface browning. Oils have around 65 ppm alkaline materials at their optimum and increase up to >150 ppm as they degrade.

The Veri-Fry TAM test kit (Libra Laboratories) is a test used to measure Total Alkaline Materials. This test is again a test tube type kit which contains an oil fraction gel with an indicator dye. The test oil is mixed with the gel at 40C and the alkaline materials are extracted into the gel and the color change is compared to a color card. If one wishes to quantify the results further, the color can be read at 412 nm using a 1 mm cuvette. The method is quick, inexpensive and does not require special training of personnel. All that is required of the operator is that they be able to distinguish colors accurately. One does have to maintain the kit at 40C during the test.

The American Oil Chemists' Society has set up a standard method for evaluating alkaline materials in freshly

refined oils. Method Cc 17-79 requires a titration to determine the amount of soaps in an oil. This method is accurate from 0 to 20ppm soaps. The use of this method in measuring the total alkaline materials in a used or degraded frying medium is severely limited because under these conditions total alkaline materials may reach as high as 200ppm.

Smoke Point - Mankel (1970) stated that if the smoke point is lower than 170 C, the oil is unsatisfactory. However, Wu and Nawar (1986) were forced to abandon the measurement of smoke points in frying oils due to a lack of reproducibility or the failure to reflect the extent of thermal abuse of the oil.

Carbonyls - These are also degradation compounds in the oil which can be correlated to total polars. However, the formation of carbonyl compounds is not necessarily a uniform phenomenon during thermal degradation.

The Fritest (Merck Inc.) is a colorimetric test kit sensitive to carbonyl compounds where the fat is saponified by exposure to sodium hydroxide in the test reagent. The color becomes darker as the oil degrades. While the test does correlate to %polars by the standard method, the test results can be influenced by type of oil and the amount of polymer in the oil (Blumenthal, 1987). The results tend to

reflect more a trend in the degradation of the oil rather than the quantification of a given attribute. The formation of carbonyls was monitored by Croon et al. (1986) in Scandinavia using the Merck Fritest colorimetric test kit. They reported reproducible results which corresponded relatively well to polar compound values. The Fritest was rapid and easy to handle, however, one sample out of five was inaccurate. Others have found the test to be subject to the problem of false positives and negatives.

Polar Materials - These are compounds which consist of a number of degradation products in the thermally degraded oil and are measured by the standard IUPAC-AOAC column chromatographic technique which is accepted in Europe as the criterion for acceptance or rejection of frying media. The measurement of polar materials is considered by many researchers to be the standard method to which all other methods are compared. The polar materials are considered by many European countries as being related to possible harmful effects of overheated fats or oils. The %polars limits for a degraded oil vary from 24 to 27% in various European countries (M.Blumenthal, personal communication). Firestone (1988) reported that 17 laboratories conducted a collaborative study on this method and reported standard deviations of 5 - 12% for samples with 5 - 10% triglyceride

polymers. While this research method appears to be excellent from a standpoint of measuring polar materials, it is too costly and lengthy to be of much use to foodservice operations or testing labs with large numbers of samples.

There currently exists a test kit method called the Veri-Fry TPM (Total Polar Materials, Libra Laboratories). According to Blumenthal (1987) it has shown good correlation to the IUPAC-AOAC method and is used by health inspectors in Europe to determine if the legal endpoint for frying oils (24 to 27% polar materials) has been reached. The colored material produced in the test can be compared to color standard cards in the field or measured using a simple table top spectrophotometer in the lab to obtain more precise measurements of polar materials.

The test kit consists of a test tube which contains aqueous potassium hydroxide, bromocresol green and ethylene glycol. The test fat or oil is added to the test tube which is held at 40C in a water bath. The polar materials are extracted with shaking into the solvent which contains the dye indicator. The resultant change in color can be correlated to %polars as determined by the standard method. The test is fast, inexpensive and no training of personnel is needed to read the color card. All that is required of the operator is that they be able to distinguish colors

accurately. If one wishes to quantify the results, the absorbance at 590 nm can be read. It should be noted that care must be taken with this method to assure that the color of the tube is read before it cools down from 40C.

Polymers - The formation of polymers in oils is directly related to the amount of time the oil is exposed to elevated temperatures. The polymer levels found in frying oils do not appear to be significantly affected by the addition of new oil to the system (Wu & Nawar, 1986) making their measurement feasible from an analytical standpoint. Polymeric materials constitute a substantial fraction of the polar materials in the frying oil (Blumenthal, 1987; Peled et al., 1975) and are not very reactive.

The method of Peled et al. (1975) has been used by a number of researchers including Wu and Nawar (1986) to ascertain polymeric materials. Other methods have also been utilized to evaluate polymers including a modification of the AOCS Official Method Ca 5a-40 (Talley et al., 1987). These methods however again represent considerable time and expense which is not feasible in testing environments where large numbers of samples are measured. A recent method in use internationally involves the use of a High Performance Liquid Chromatograph (HPLC) with a gel permeation column. It has been developed as Draft NEN 6348 for adoption as an

IUPAC method. The method requires minimal preparation of the test samples, but does involve some skill on the part of the researcher in setting up oil standards and the HPLC conditions. This makes it more suitable for research laboratories.

However, once the HPLC is set up, a large number of samples can be run. In addition, the present method for polymers does not permit refined quantification of polymers.

Foodoil Sensor (FOS) - The FOS method has been used by a number of researchers to evaluate the quality of frying oils. The method involves the measurement of changes in dielectric constant in the frying oil using an electronic device (Foodoil Sensor Model NI-20, Northern Instruments Corporation, Lino lakes, MN).

Smith et al. (1986) reported good correlation between changes in FOS values and the accumulation of polar materials and stated that it was the most convenient method for quality control in foodservice environments. Croon et al. (1986) reported that the FOS method had the highest correlation to the standard polar materials method. They stated that it was easy to operate and one could complete an assay in 10 - 20 minutes. The disadvantages of the device, according to Croon et. al. (1986) was that it must be calibrated with fresh oil of the same type as that being

tested and that it was quite sensitive to air draughts when used next to a hood or window.

Wu and Nawar (1986) reported that the FOS method by itself did not always agree with other parameters of frying oils but that when FOS values were used as part of a polymer/FOS ratio, one could adequately predict quality of the frying oil. Another advantage of the FOS method is that it is not affected by replenishment of the frying oil (Wu & Nawar, 1986).

The foodoil sensor is an instrument which measures changes in the dielectric constant of heated oils. The dielectric constant of a substance is its ability to transfer electrical energy as compared to a vacuum. This method has been used by a number of researchers to evaluate the quality of cooking oils (Fritsch et al., 1979; Paradis & Nawar, 1981; Graziano, 1979). The instrument is a compact unit, relatively inexpensive, is simple to operate and requires only a few drops of oil for each measurement. Sample testing consists of zeroing the instrument with a standard or unused oil sample, then measuring the dielectric change between the standard/unused oil and the used frying fat. This analysis takes between three to five minutes to complete. As the shortening breaks down, peroxides, acids, and other radicals are formed on the shortening molecule.

These cause the molecule to become somewhat polar. As the number of polar molecules increases, the dielectric constant of the shortening mixture increases. Tests conducted by a number of researchers (Paradis & Nawar, 1981; Fritsch et al., 1979; Graziano, 1979; Smith et al., 1986; Croon et al., 1986) with this instrument showed that oxidation products were primarily responsible for changes in the dielectric constant. Fritsch et al., (1979) showed this by running regression analyses between instrument readings and other analytical procedures. Total polar materials (TPM) and a decrease in iodine values yielded the highest correlations (.991 and .947). Free fatty acids yielded a much lower correlation (.569). This indicates that the change in dielectric constant measures primarily deterioration due to oxidation and not hydrolysis. Fritsch, et al. (1979) states that this is desirable, as the extent of hydrolysis during frying can vary without significantly affecting product quality. A number of other researchers (Wu & Nawar, 1986; Smith et al., 1986; Croon et al., 1986) have also found similar correlations between Foodoil Sensor readings and polar materials, which were analyzed via the official IUPAC - AOAC methods. The IUPAC - AOAC method for analysis of polar materials has also been correlated to a test kit, the Veri FRY TPM test kit, produced by Libra Laboratories.

One possible limitation of the Foodoil sensor is based on the fact that different fresh fats have different dielectric constants. The more saturated fats tend to have lower values than the more highly unsaturated fats. This limitation is taken care of by calibrating the Foodoil Sensor with a fresh, unused sample of the oil to be used in the frying operation. Fritsch (1979) states that during the frying of some foods, some of the fat in the food is extracted into the frying fat. If the food fat has a lower dielectric constant than the frying fat, a negative reading would be obtained. If the food fat has a higher dielectric constant than the frying fat, the reverse would be true. Paradis and Nawar (1981) state that water can also be extracted from the food into the cooking medium and may lead to spurious results. For this reason oil samples should not be taken from the fryer while the food is being fried. The operator's manual states that the Foodoil Sensor should not be operated near draughts. This could be a problem in a restaurant setting, but could easily be remedied. Some considerations which could lead to problems when using this method are:

1 - it must be calibrated using the fresh oil of the same type.

2 - oil-blanched foods might introduce other oils into the frying medium being evaluated.

3 - any water in the oil being measured will cause many problems in getting meaningful measurements. One should dry the oil in a oven before measuring and this could affect the dielectric constant.

4 - the instrument is sensitive to air currents in the room from open doors or windows.

5 - a number of studies have indicated that the instrument has to be warmed up for up to 4 hours.

6 - the instrument measurements can be influenced by the heat of the test oil prior to analysis. The hotter the oil the more precise the replicate measurements on the same sample.

CHAPTER 2

JOURNAL ARTICLE

Authors Title Page

DETERMINATION OF FRYING MEDIUM

QUALITY LIFE

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ABSTRACT

DETERMINATION OF FRYING MEDIUM QUALITY LIFE

Various quick assay methods which are currently available were used to determine the quality life endpoint of a frying medium. French fries were fried for 21 days (12 hours/day). Samples of french fries and frying medium were taken every 2 hours. Sensory panels were conducted twice a day. Endpoints for the frying medium based on each assay method were then calculated and compared to the sensory endpoint of the french fries. The results indicated that the various assay methods, including %Polars, %Free Fatty Acids, dielectric constant and color, all linearly increased with time. However, the assay methods indicated very different endpoints based on accepted food industry limits. While the french fries lost sensory acceptance based on greasiness by day 15 of the study, the %FFA endpoint was 7 days, %polar materials kit was 17 days and the dielectric constant was 20 days. The french fry moisture and fat contents did not significantly change with time although the perception of greasiness did increase for the sensory panel. It is hypothesized that the deposition of the fat changed so that more was deposited on the surface of the fries as the frying medium degraded.

INTRODUCTION

Deep fat frying is one of the most commonly used procedures for preparation and manufacture of foods (Olieman, 1983; Chang et al., 1978). In deep fat frying the food is completely surrounded by the frying medium. The frying medium acts as a heat transfer medium. The higher temperatures possible with deep fat frying result in a more rapid heat penetration, therefore making it a more efficient method than the dry heat of the oven or boiling in water (Stevenson et al., 1984). Since the use of deepfat frying as a means of food preparation is so wide spread in the food service industry, methods to effectively monitor the process of deep fat frying are essential. The objectives of this study were:

1) to evaluate various quick assay methods for measuring thermal degradation in a commercial frying medium under realistic industry conditions,

2) provide information on days of quality life as measured by the different assay methods based on published criteria,

3) to correlate the days of quality life for the frying medium as measured by the objective measurements with the upon sensory test results for french fries prepared in the frying medium,

4) recommend a quick assay method for measuring the thermal degradation of frying media based on ease of use and correlation to sensory test results, and

5) to compare thermal degradation in two fryers with different fryer design.

The results of this study will contribute to the available information on methods used to monitor the degradation of frying media in foodservice environments.

LITERATURE REVIEW

During the thermal degradation of frying media the lipids involved become thermally oxidized to produce a number of decomposition products (Nawar, 1985). Oils deteriorate more or less slowly depending on the amount of heating and the type and amount of food fried.

During the thermal degradation of frying media, an induction period is followed by the formation of peroxides and their subsequent decomposition to other products. As peroxide levels increase, the oxygen level in the frying medium also increases. As polymerization and viscosity of the frying medium increase, more breakdown products accumulate.

There are numerous degradation products formed during the thermal degradation process. These products include a series of aldehydes, ketones, acid esters, alcohols,

hydrocarbons, lactones, cyclic compounds, dimers, and polymers. The relative amounts of these compounds can vary widely depending on the nature of the substrates and the parameters of the heat treatment. The principal reaction pathways involve the formation and decomposition of hydroperoxide intermediates with similar qualitative patterns (Frankel, 1979). The formation and destruction of these hydroperoxides is extremely rapid at high temperatures as are the resulting primary decomposition products which undergo further oxidative decomposition. As the oxidative process continues, a number of reaction mechanisms can occur which result in the development of hundreds of compounds (Chang & Paulose, 1973; Chang et al., 1978; Frankel, 1982; Selke et al., 1975, 1980; Nawar et al., 1977). Food aerates the oil during cooking providing oxygen which can then cause the oxidation of the oil to produce hydroperoxides. The hydroperoxides can then undergo: 1) fission to produce alcohols and aldehydes which degrade to acids and hydrocarbons, which with heating, form dimers and cyclic compounds, 2) dehydration to ketones, or 3) can form free radicals which can form dimers, trimers, epoxides, alcohols or hydrocarbons which are polar in nature.

The food can contribute both colored compounds (fat soluble pigments) as well as lipids (food fats/oils) to the

frying system. It is also important to remember that the frying operation is a dehydration process taking place at the food frying medium interface. Steam is generated which can carry off degradation compounds (volatile compounds) already formed in the frying oil as smoke or can hydrolyze the frying oil into free fatty acids, di - glycerides, mono - glycerides and glycerol. Pai et al. (1979) showed that the presence of water during heating resulted in substantial hydrolysis of the frying oil. This was seen as an increase in the amounts of C6 - C14 even numbered free fatty acids.

MATERIALS AND METHODS

Materials. The frying media used in the study was an all vegetable partially hydrogenated soybean oil. The frying media contained tert-Butyl hydroquinone as an antioxidant. French fries used in the study were Simplot 1/4" Blue Ribbon shoestring potatoes (Grade A, Extra Long Fancy, #46420). These french fries were stored at 0 F in the freezer until tested. At the end of each day of frying, the frying medium was cooled for 10 - 15 minutes and then filtered using the Frymaster PF Portable filter, Filter magic filter paper, and a filtering aid consisting of diatomaceous earth, crystalline silica, quartz, and cristobalite.

Experimental Design. The frying medium life determination was conducted under commercial conditions. Thirty-two 31b.

loads of french fries (Simplot 1/4" fry) per 12 hour day (2 baskets/fryer = 1.5lb. loads/basket) were fried in two different types of fryers for twenty one days (we are unable to reveal the fryer designs at this time due to funding restraints). Each fryer contained 50 lbs. of frying medium. Each french fry load was fried for 2 minutes 45 seconds at 350 F to obtain a 30% moisture loss in a vegetable frying medium (Melfry). The frying medium was permitted to return to 350 F between french fry loads. The same frying medium was used throughout the test. Fresh MelFry was used as make up at the end of each operating day. Actual addback amounts were recorded and mean addback amounts were calculated over the period of the study.

The temperature was constantly monitored via thermocouples placed in the fryer. The thermocouples then transferred the data to a computer which displayed and recorded the temperature of the fryer throughout the study.

Four ounce samples of frying medium were taken at 10 AM and 2 PM each day of the study. Each sample of frying medium was assayed in triplicate for 1) free fatty acids by the standard AOCS method, 2) change in dielectric constant (Foodoil Sensor, Model NI-20 Northern Instruments), 3) total polar materials using the Veri-Fry TPM test kit (Libra Laboratories) and 4) spectrophotometric color changes by the

AOCS proposed method. Rate constants based on the linear regression equations of changes in the frying medium based on each assay method versus time were obtained. Correlation coefficients of these relationships were calculated to determine the relationship of time to changes in the oil. Pearsons correlation coefficients for linearity between assay methods were also calculated to determine how the methods correlated to each other.

Four ounce samples of french fries were taken twice daily at 10 AM and 2 PM for the twenty-one day period. The samples were packed in moisture impermeable glass jars and stored at 0 C until analysis. Each french fry sample was assayed in at least duplicate for %Moisture (AOAC moisture determination) and %Crude Fat (AOAC standard method Soxlet analysis). The relationship of moisture and fat changes to time were determined by linear regression.

Frying Medium Life Determination Test Method. The fryer was loaded with the frying medium, MelFry, to the level of the fill line, approximately 50 lbs. of frying medium. The same frying medium was used continuously throughout the test. Fresh frying medium was added at the end of each day's run to the fill line in the fryer. The amount of frying medium added back at the end of each day was recorded in pounds.

At the beginning of each day of the study, the frying medium was allowed to come up in temperature to 350 F for the fryer. The fryer was then allowed to stabilize for one hour.

The french fries were held at 0 C in a freezer in the test area prior to cooking. The temperature of the french fries during storage was monitored throughout the study to assure they were at 0 C before cooking. 0 C fries were removed from the freezer and weighed into 1.5 lb. loads. They were weighed into plastic containers and again placed in the freezer at 0 C overnight until use. The french fries were loaded into a pair of baskets (1.5 lbs./basket). The fries were taken from the freezer and immediately placed into the baskets. The pair of baskets were then simultaneously lowered into the fryer.

The daily frying schedule was based on a cook time determination test run prior to the frying medium life determination. From this test it was determined that a cook time of 2 minutes 45 seconds was adequate to produce a 30% weight loss in each three lb. load. During the test, each three lb. load was cooked for 2 min 45 sec and then weighed after a two min drip period. The french fries were not drained over the frying medium, as this could lead to changes in french fry composition due to the possible

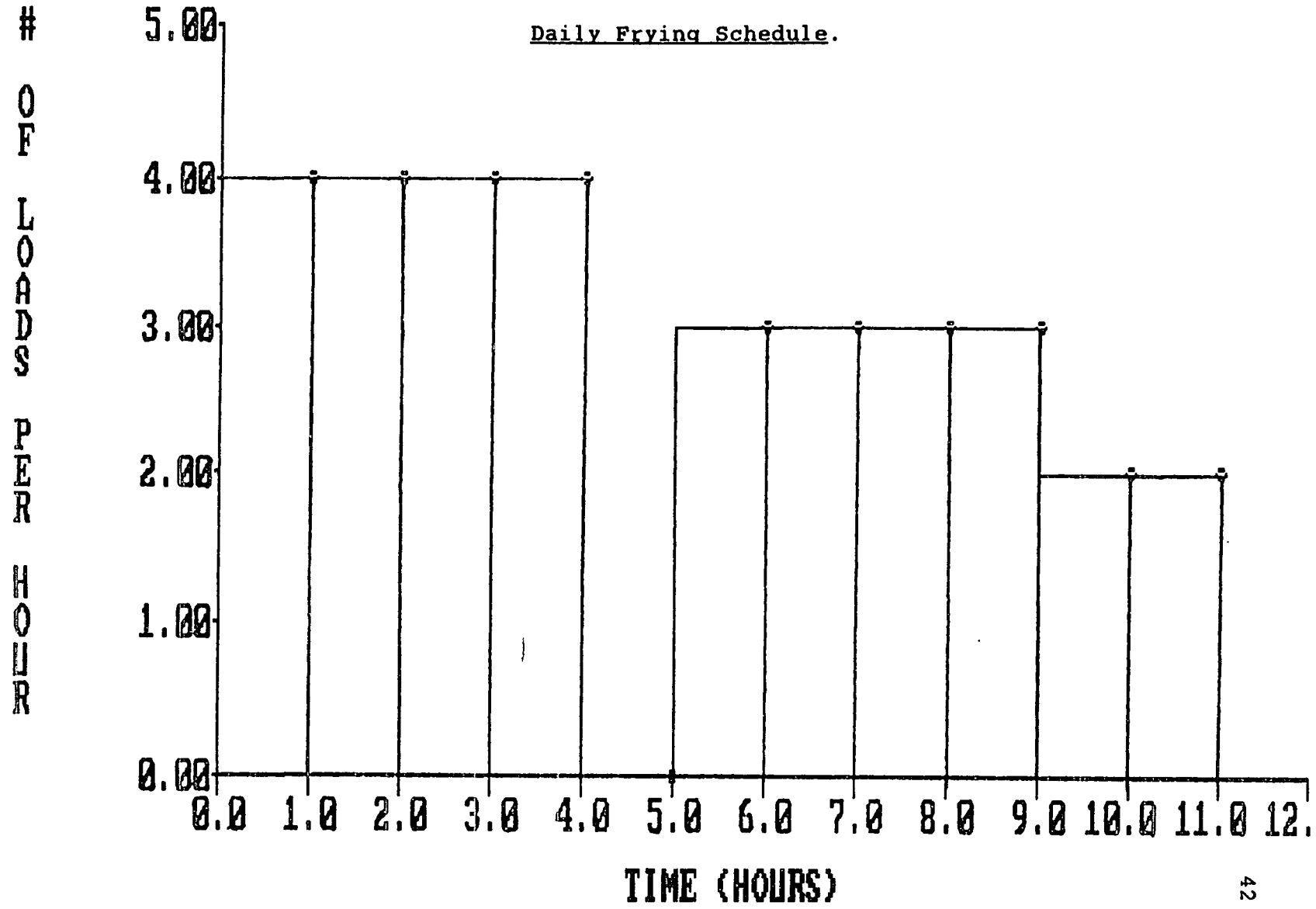
uptake of steam evolving from the surface of the frying medium. The number of loads fried per hour was based on a realistic restaurant situation. The daily frying schedule used in this experiment is shown in Figure 3. Care was taken to space the loads cooked per hour throughout the hour so that each fryer had ample time to return to the 350 F operating temperature before another load of fries was introduced. In the case of the four load hours this meant that for each fryer, a load was fried every fifteen minutes, for the three load hours a load was fried every twenty minutes, and for the two load hours, a load was fried every thirty minutes.

Methods. Frying medium was added back to each fryer at the end of each day of frying. The amount of frying medium added back to each fryer was determined by weighing a container of the frying medium before and after the addition of frying medium to each of the fryers. The difference was recorded as addback for each fryer. The amount of frying medium added back to each fryer was recorded daily.

The method used to analyze Free Fatty Acids in the frying medium was the standard titrimetric method (AOCS Ca 5a-40) used by a number of others (Talley et al., 1987; Wu & Nawar, 1986). A few drops of the frying medium is added to a 250ml Erlenmeyer flask containing 50ml 95% ethyl alcohol

Figure 3.

Daily Frying Schedule.



and a few drops of phenolphthalein to neutralize the alcohol. A weighed sample of frying medium is then added to the flask. This mixture is then titrated with 0.1N sodium hydroxide solution. The volume of sodium hydroxide required to produce a permanent pink in the supernatant alcohol is recorded. Each whole number (1.0ml) is equal to 0.1% free fatty acid. The best results are obtained when hot oil samples are used.

The method used for analysis of color was a variation of the AOCS Official Method Ca 13c-50. In this method, the color of the frying medium was measured at several wavelengths against a blank of unused frying medium (Melfry). The absorbances at four wavelengths (670nm, 620nm, 550nm, and 460nm) were then introduced into an equation and an empirical color index was derived.

The method used to analyze Total Polar Materials in the frying medium was the Veri- fry TPM Diagnostic Test Kit. The test kit tube containing a light blue gel was first placed in a 40 F water bath to melt the gel. Warm frying medium is then placed into the test kit tube. The tube is fitted with a screw cap which is then screwed on tightly. Shaking the tube for a short time mixes the contents of the tube. The tube is permitted to stand for 30 seconds to allow the reaction to occur. A color is produced in the tube which

can be matched to a color standard card provided with the test kit. The colors on the standard card correspond to varying levels of %polars. Blumenthal (1987) showed excellent correlations between this test kit and the standard method for polar materials.

The changes in Dielectric Constant for the frying medium were measured using the Foodoil Sensor model NI 20 (Northern Instruments, Lino Lakes, MN.). This instrument was operated according to the method of Fritsch et al. (1979). The instrument required a warm up period (up to four hours) with stored samples. The instrument did not require as much warm up for samples that were taken directly out of the fryer.

French Fries were also evaluated twice daily by a sensory panel consisting of 5 to 7 PG&E Learning Center office personnel who were not involved with the study in any way. The panel members were instructed on how to rate the products and how to fill in the sensory evaluation form. The evaluation forms asked each panelist to rate the color of the fries from 1 (White) to 10 (Dark brown with Black Flecks) and the greasiness of the fries from 1 (Not Greasy) to 5 (Very Greasy). In addition, each panelist was asked to state whether the color and degree of greasiness was acceptable or unacceptable.

During each tasting session, the panel members evaluated french fries which had been sampled immediately after the two minute drip period. The french fries from both fryers were placed on identicle white plates and placed in a small, quiet room adjacent to the test area under identicle lighting and temperature conditions. Care was taken to ensure that the fries were similar in temperature at the sampling times. On two occasions when this could not be assured due to panelist unavailability, the data were discarded as invalid. The sensory data acceptability data were used to determine when the fries were found by a majority of the panelists to be unacceptable.

RESULTS AND DISCUSSION

Addback Amounts to Fryers During the Study. One area of concern when evaluating the progress of thermal degradation is that any dilution of the frying medium, due to the addition of fresh, undegraded frying medium, be monitored. It is interesting that none of the studies in the literature, which have examined thermal degradation in frying media, have documented actual addback amounts of oil although they have reported adding fresh frying media to degraded frying media during the process of thermal degradation.

Table I shows the addbacks of frying medium for the study. Day 5 and Day 12 show somewhat higher addbacks. These higher addbacks are due to the storage of the degrading frying medium in other containers with some loss of frying medium in the storage containers. It should be noted though that even on these days the addbacks are 20% which is well within the 15 to 25% average addbacks encountered in institutional frying conditions according to Weiss (1983). It is also important to note that the sampling of the frying medium only contributed 1.5# per day to the total addback, the bulk of the addback being due to normal operating procedures. The mean values for addback in the two fryers, also shown in Table I, are around 7 1/2 lbs. and are very similar for the two fryers. They are not significantly different from each other based on student's t test and do not change significantly with time based on linear regression analysis.

Thermal Degradation Changes As Measured by Assay Methods. The best fit linear regression lines of the thermal degradation changes as measured by development of free fatty acids, increase in dielectric constant, increase in %polars and increase in color can be used to derive zero order rate constants with confidence limits for each of the assay methods. These zero order rate constants are shown in

Table I
Amount of Frying Medium Added
Back (in pounds) at the end of each Day of Frying

Day	FRYER 1	FRYER 2
1	5.95	3.65
2	6.18	8.15
3	8.43	7.40
4	8.65	10.79
5	10.11	10.09
6	7.37	6.41
7	7.46	7.50
8	8.20	8.04
9	8.03	7.11
10	9.76	8.45
11	7.16	8.23
12	10.02	12.25
13	3.76	3.95
14	8.56	8.73
15	7.79	7.17
16	6.12	7.07
17	7.40	8.53
18	5.90	5.40
19	7.61	7.22
20	6.63	7.23
MEANS	7.55	7.67

a - The means between the two fryers were not significantly different based on Students T-test.

b - Changes over time are not significantly different.

Table II for both fryers.

Several things can be noted in Table II. First it is apparent that the rates for the assay methods are higher for Fryer 2 than for Fryer 1. However when the means of the changes for the assay methods were compared using the student's t-test as is shown in Table III, there was no significant difference for thermal degradation changes as measured by any of the assay methods. Since the ranges for the assay methods for both fryers were similar, the student's t-test is a reliable test for comparing changes over time for the two fryers.

Second, it is also clear that, while the rate constants for the %polar changes are similar for the color card and absorbance measurement methods, the range for the absorbance at 590 nm method is unacceptable. It is hypothesized that the large range is due to particulates in the cuvettes which was particularly bad at the beginning of the study when the absorbance values were lower. In the future it is recommended that the degrading frying medium be filtered through glass wool rather than filter paper prior to being added to the test kit test tubes. Because of this unacceptable range, only the %polars based on card values were used to calculate endpoints for the frying medium.

It should be noted that the assay techniques showed

Table II

Zero Order Rate Constants for Changes in Frying Medium as Measured by Different Assay Methods

Assay Method	FRYER 1	FRYER 2
Free Fatty Acids	0.49 +/- 0.02%/day	0.63 +/- 0.02%/day
Foodoil Sensor	0.14 +/- 0.006/day	0.16 +/- 0.006/day
Color	2.24 +/- 0.09/day	2.72 +/- 0.09/day
% Polars (Based on card#)a	1.16 +/- 0.04%/day	1.40 +/- 0.03%/day
% Polars (Based on abs.)b	1.07 +/- 1.1%/day	1.41 +/- 1.4%/day

a - Rate constant based on 15 days when color cards reached value of 5 and stayed there.

b - Rate constant based on 21 days - problems with haziness in spectrophotometer cuvette.

Table III

Means for Changes in Various Assay Methods in the Two Fryers

Assay Method	FRYER 1	FRYER 2	
FFA (AOCS method)	3.87	5.24	NS
Foodoil Sensor	1.68	2.01	NS
% Polars (based on card#)	11.17	12.15	NS
(based on abs.)	13.92	15.62	NS
Color	18.26	22.19	NS

The symbol NS stands for no significant difference using Students T test.

general variability around the best fit lines with the exception of the free fatty acid data. In the case of the free fatty acids, although there were very high correlations to the linear line, there was a similar and definite trend for the actual free fatty acid measurements for both fryers. An initial lag of values was followed by a sharper increase of values which was in turn followed by another leveling off of increases. It has been noted (Gerald DeMenna, personal communication) by other researchers that free fatty acids demonstrate increases to a given level and the subsequent condensation to other thermal degradation products which is seen as a leveling off of free fatty acid values. Croon et al. (1986) reported poor correlation of free fatty acids to quality of frying medium in 100 frying medium samples collected from fast food restaurants. Wu and Nawar (1986) reported increases in free fatty acids with time but commented that the free fatty acids were affected by dilution due to frying medium addbacks. The results for this study indicate good agreement to the linear regression line with indications that the free fatty acids could be increasing, condensing to other thermal degradation products and then increasing again. It is possible that the results for this study differ from the results of earlier studies because of the tight control of the test conditions in the

present study and to the presence of a uniform food test material. In the Croon et al. (1986) study, the frying media evaluated were from various fast food restuarants with no control on thermal degradation conditions. In the study conducted by Wu and Nawar (1986) corn oil was degraded at 185 C by itself with no food present.

Table IV lists the linear regression correlation coefficients for the assay methods versus time and each other. It is evident that all the assay methods had excellent correlation with time which means that they changed linearly with time and that the rate constants derived from the linear regression best fit lines are valid. The methods increased linearly with respect to each other with excellent correlations between dielectric constant and free fatty acids and very good correlations between dielectric constants and %polars as well as free fatty acids and %polars. The method which correlated least with the other methods was the color method. While the color method increased linearly with time, there were problems in the color method due to particulates and haziness in the degrading frying medium. It should be kept in mind, however, that although the correlation coefficients between methods may indicate good linearity with respect to each other, one must still calculate times to endpoints for the frying medium based on each assay method if one wants to

Table IV

Correlation Values for Assay Methods
Versus Time and Each Other

	TIME FRYER 1/FRYER 2	FFA	Foodoil Sensor	Color	% Polars card#	% Polars Abs.
FFA	.971/.976	1.000	.964	.883	.903	.947
FOS (Foodoil Sensor)	.963/.973	.982	1.000	.907	.900	.926
Color	.898/.980	.966	.972	1.000	.786	.858
%Polar (Based on Card#)	.991/.987	.958	.940	.976	1.000	.890
%Polar (Based on Absorbance)	.957/.974	.965	.960	.975	.923	1.000

NOTE: Values for Fryer 1 are above the line and values for Fryer 2 are below the line, with the exception of values reported for time.

compare the methods in a meaningful way.

In addition to determining the linearity of the %polars based on color card and absorbance measurements, it was decided that the %polars for the two quick methods needed to be correlated to actual %polars as determined by the standard IUPAC-AOAC method. With this in mind, seven samples of frying medium from each fryer over the study period were sent to Gerald DeMenna, Libra Laboratories. The samples were sent blind so that there would be no bias on the part of Libra Laboratories. The results from the %polars standard method were then used to establish standard curves for the quick polars test kits using both the color card and absorbance methods. The correlation coefficients for these standard curves are shown in Table V and show excellent agreement between the standard method and the quick test kit.

Changes in French Fries. While there are very slight changes in %moisture and %fat as indicated by the linear regression lines, linear regression analysis revealed that the changes were not significantly different than zero. In other words, the %moisture and %fat for the french fries did not significantly change as the frying medium degraded. These findings appear to contradict numerous observations that products seem greasier as frying media degrade. The

Table V

Correlation of % Polars based on Card# and Absorbance to % Polars determined by IUPAC/AOAC Method

	Correlation Value
% Polars (card#)	.980
% Polars (abs.)	.930

lack of significant changes may be explained, if one assumes that the increase in surfactants in the frying medium as it degrades could result in differences in the way that the frying medium interacts with the surface of the food. While increased surfactant levels can result in better penetration of the frying medium into the surface of the food, especially in batter covered products, the surface temperature of the food will also tend to rise because the frying medium can come into better contact with the food surface. In a food like french fries, which have a smooth surface with an ample amount of starch present which can undergo gelatinization and subsequent film formation, the penetration of the frying medium due to increased surfactant levels could be counter balanced by the resistance to penetration as a result of more rapid film formation at higher food surface temperatures.

The sensory evaluation scores for percent acceptability based on color and greasiness of the french fries are shown in Figures 4 to 7. The numeric ratings for color and greasiness did not change significantly with time so that only the %acceptability scores are presented here. The percent acceptability scores for color remained unchanged for Fryer 1 and increased somewhat for Fryer 2. The color therefore was assumed to not have an influence on negative

Figure 4

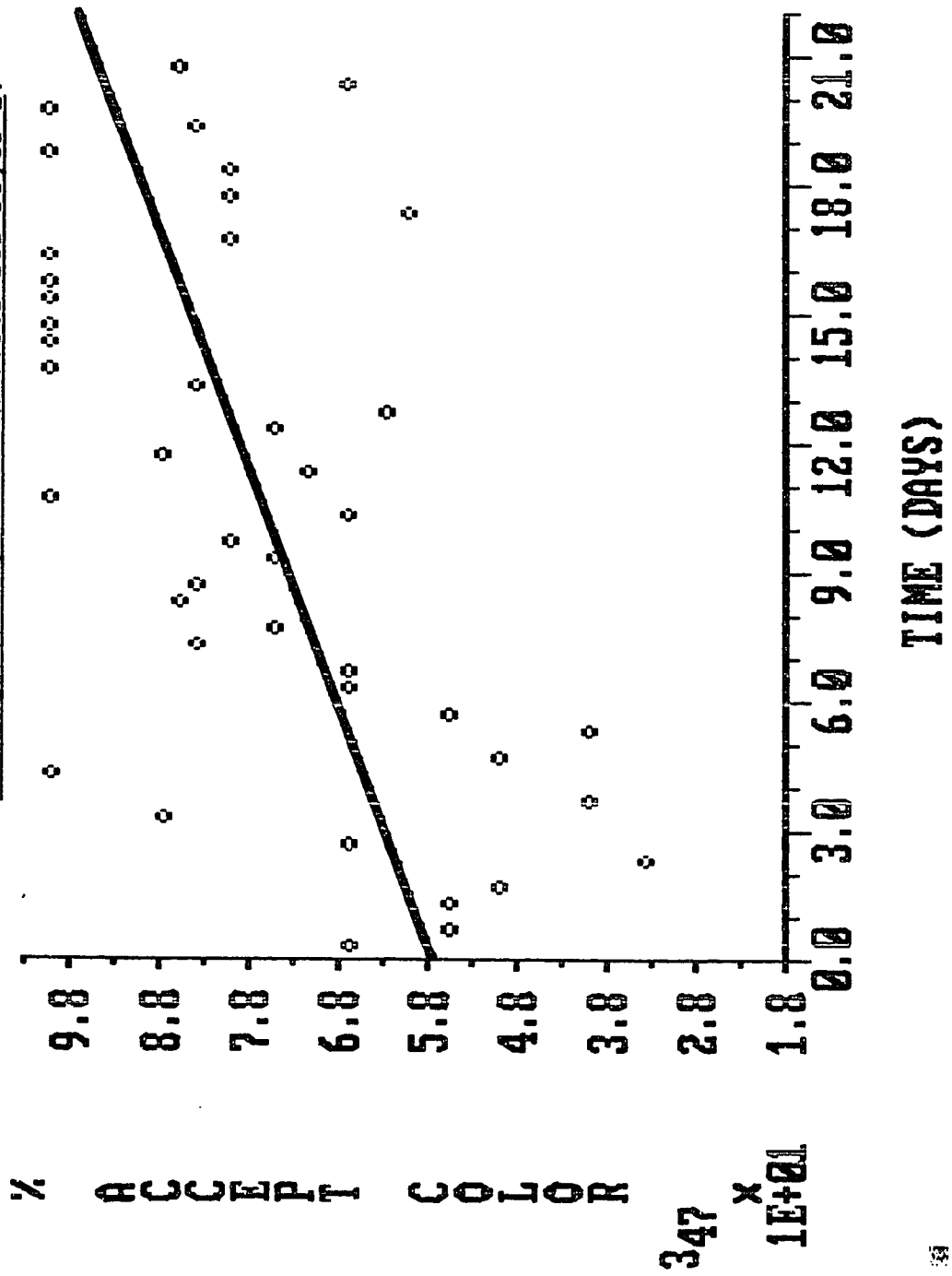

% Acceptability Based on Color for Fryer 1.
% ACCEPT COLOR
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
3.0
6.0
9.0
12.0
15.0
18.0
21.0
TIME (DAYS)
342 x 1E+01

Figure 5

% Acceptability Based on Color for Fryer 2.

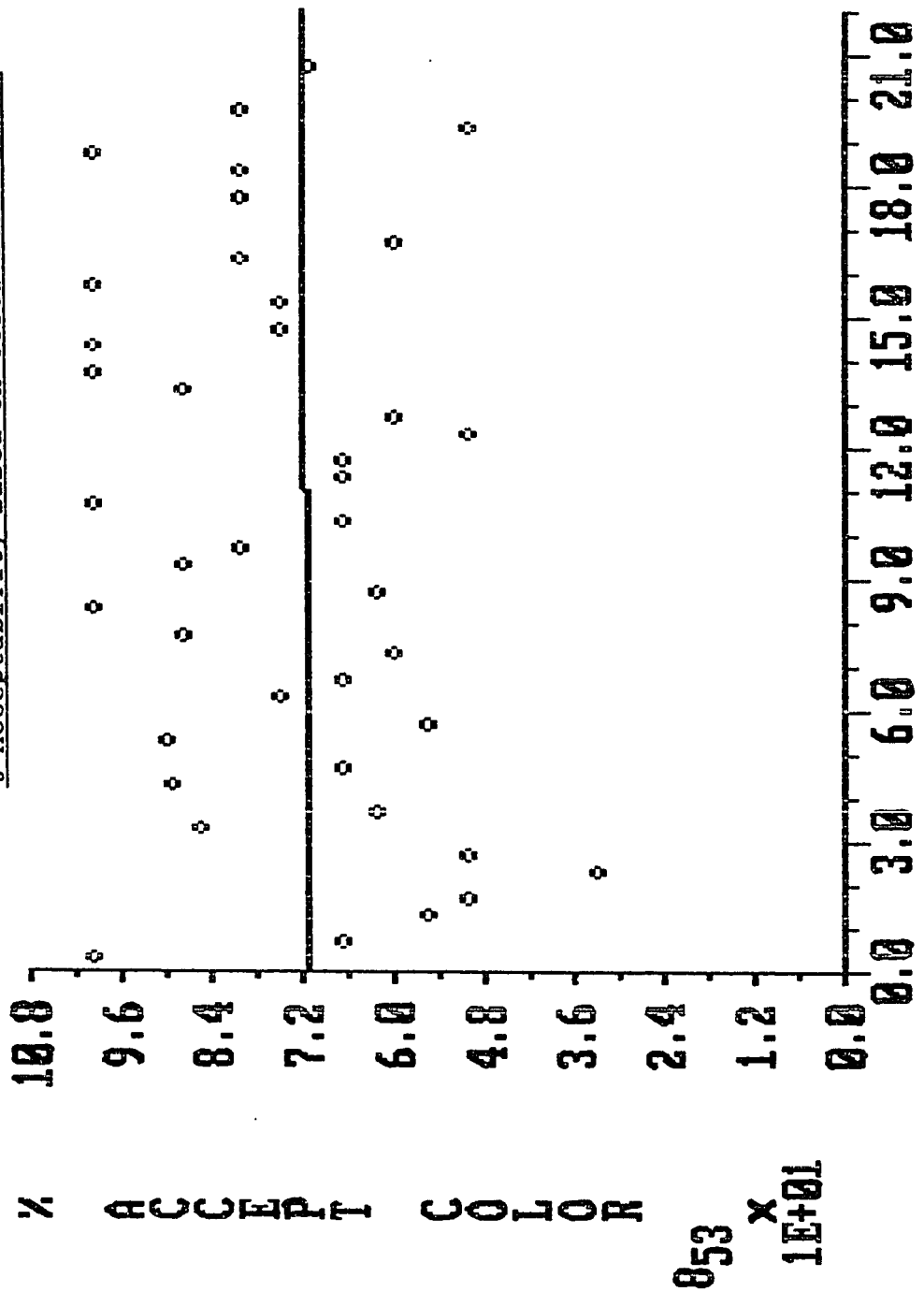


Figure 6

% Acceptability Based on Greasiness for Fryer 1.

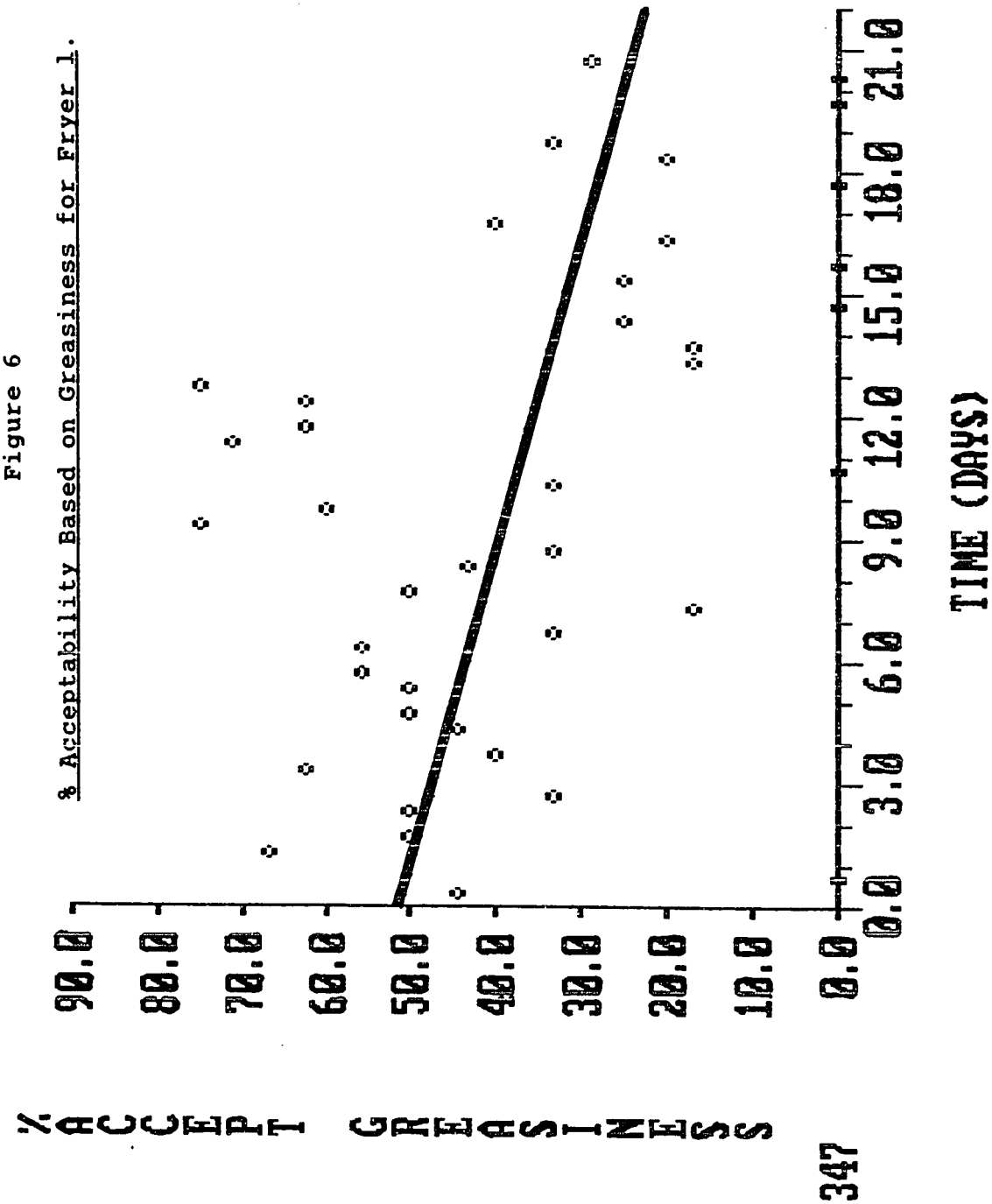
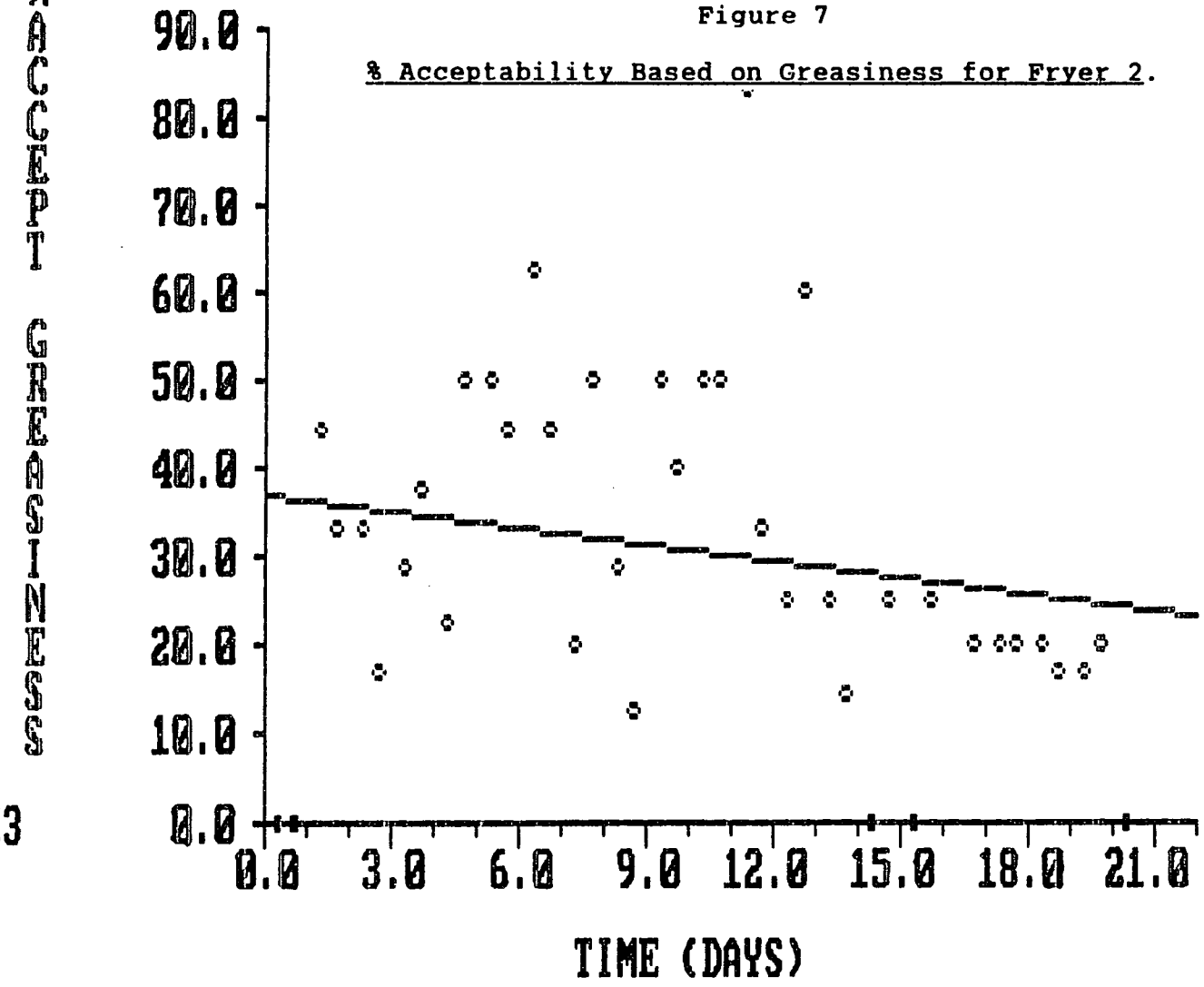


Figure 7

% Acceptability Based on Greasiness for Fryer 2.



sensory changes of the frying fries as a consequence of degrading frying medium. In contrast, the % acceptability scores for greasiness of the french fries for both Fryer 1 and Fryer 2, had decreased to a plateau around 30 to 40% by the 15th day of the study as can be seen in Figures 6 and 7.

Due to the variability of the data, the correlation coefficients for the best fit lines are low. The low variability could be due, in part, to the intrinsic variability of sensory analysis. However there was also limited control during the test over the temperature of the fries being tasted. The taste panel consisted of PG&E office personnel who were not always immediately available for the sensory test. Thus, some of the perceived differences in the relative acceptability of the fries could have been influenced by the time elapsed between frying and tasting. Based on this, the sensory data can only provide a general indication of relative acceptability of the fries rather than a precise endpoint.

Table VI lists the rate constants in terms of %acceptability change per day as well as the correlation coefficients for the lines. It is evident that during the first fifteen days the fries decreased in acceptability. From day 16 to day 21, the fries either continued to

Table VI

Rate Constants and Correlation Coefficients
For % Acceptability Based on Greasiness

	FRYER 1	
	Rate Constant	Correlation Coefficient
days 1 - 15	- 0.721 %/day	.146
days 16 - 21	1.000 %/day	.071
	FRYER 2	
	Rate Constant	Correlation Coefficient
days 1 - 15	- 0.657 %/day	.148
days 16 - 21	- 0.462 %/day	.065

decrease in acceptability at a slower rate for Fryer 2 or to increase slightly for Fryer 1. Due to the variability of the data, the correlation coefficients for the best fit lines are low. The low variability could be due, in part, to the intrinsic variability of sensory analysis. However there was also limited control during the test over the temperature of the fries being tasted. The taste panel consisted of PG&E office personnel who were not always immediately available for the sensory test. Thus, some of the perceived differences in the relative acceptability of the fries could have been influenced by the time elapsed between frying and tasting. Based on this, the sensory data can only provide a general indication of relative acceptability of the fries rather than a precise endpoint.

Endpoints of Assay Methods.

Table VII lists the days of quality life of the frying medium based upon theoretical endpoint levels of free fatty acids, dielectric constants and %polars. These theoretical endpoints were taken from the literature or regulatory statutes where the level for free fatty acid was based on the USDA maximum, the level for dielectric constant was based on a number of studies in the literature and the level of %polars was based on the legal limits of 24% to 27% polars in Europe. The days of quality life are derived from

Table VII

Comparison of Time to End of Quality Life of a Frying Medium for Various Assay Methods

Assay Method	Theoretical Endpoint Level[a]	Days of Quality Life Fryer 1	Fryer 2
FFA (AOCS method)	2.0%	6.7+/-0.3	5.3+/-0.2
Foodoil Sensor	3.0 units	20.3+/-0.8	16.7+/-0.6
% Polars (based on card#)	24%	18.5+/-0.5	15.9+/-0.5

a Times to end of quality life are based on theoretical endpoints generally accepted in literature and on linear regression equations for the study.

the linear regression analysis of changes in the assay values with time. Several things are evident from Table VII.

First, it is evident that depending upon the theoretical endpoint used the projected days of quality life are radically different for the free fatty acids versus the dielectric constant and the %polars. This discrepancy in days of quality life can be explained if one realizes that the 2% limit for free fatty acids is based upon problems with subsequent oxidation during storage of fried foods and does not indicate that the frying medium itself is unacceptable or that it will produce unacceptable fried products if the fried products are immediately consumed. Indeed, the frying medium can contain up to 6 to 8% free fatty acids before a trained or semi-trained panel will find it unacceptable (R. Stier, personal communication). This observation is borne out by the fact that the sensory panel in this study did not find the product unacceptably greasy until 13 to 15 days.

The other thing that can be noted from Table VII is that the dielectric constant days of quality life based on theoretical endpoint were considerably longer than the sensory days of quality life. This fact, in addition to the numerous problems we encountered using the Foodoil Sensor

which are outlined above in the discussion of quick methods, made this method less valuable as an indicator of frying medium quality life. The days of quality life for the %polars test kit by the color card method exceeded the sensory days of quality life somewhat, but were not significantly different.

For the free fatty acids, the levels were from around 6 to 8%, for the %polars the levels were from around 20 to 23% and for dielectric constant the values ranged from 2.3 to 2.7. What this means is that by the time the sensory panel first definitely found the french fries unacceptable, the fatty acid levels were in the range noted by R. Stier as being detectable by semi-trained panels.

The levels of %polars at Day 15 were slightly below the European legal limit range of 24-27%. What is interesting about the %polar results, however, is that while the levels for the %polars were from 20 to 23% at Day 15, the color card readings were from 4.5 to 5.0 by Day 15. On a scale of 1 to 5, the manufacturers of the polar kit recommend discarding frying media used in restaurant service when the card color reaches 5.0.

The dielectric constants were lower than the values cited in the literature for end of quality life of frying media. In addition to the problems encountered in our

laboratory in getting uniform readings for the same sample, the dielectric constant readings change depending on the oil and any oil introduced into the fryer by the fried foods. The facts need to be considered if the Foodoil Sensor is to be used for determining frying media thermal degradation.

CONCLUSIONS

The results of this study indicate that the various assay methods all increased linearly with time. The assay methods also had good to excellent linear correlation with each other with the exception of the color method. Statistical analysis revealed that the changes in the assay methods were not significantly different for the two fryers although Fryer 2 showed greater changes than Fryer 1. The %moisture and %fat for the french fries did not change significantly with time. The acceptability of the french fries based on greasiness did decrease as the frying medium degraded.

Based on these conclusions, it is recommended that the % polars test kit be used in actual institutional use to test its validity as an indicator of frying medium quality life. The dielectric constant (Foodoil Sensor) can also be used to gauge changes, but the polar kit is necessary to determine actual endpoints for quality life. It is recommended that the frying media be discarded when the

color card readings for the polar kits are at the 5.0 level. A further note is that care should be taken that the operators using the kits should be able to discern colors.

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Chapter 3

SUMMARY AND RECOMMENDATIONS

Summary

Samples of a frying medium (MelFry) used to prepare French Fries were evaluated using various quick assay techniques, as well as by a semi-trained sensory panel. In each analysis, undegraded frying medium was used as a control. The results of this study indicated that all of the various assay methods tested increased linearly with time. The assay methods also had good to excellent linear correlation with each other with the exception of the color method. Statistical analysis revealed that the changes in the assay methods were not significantly different for the two fryers although Fryer 2 showed greater changes than Fryer 1. The %moisture and %fat for the french fries did not change significantly with time. The acceptability of the french fries based on greasiness did decrease as the frying medium degraded. The days of quality life for the french fries were from 13 to 15 days as determined by the sensory panel. The %polar test kit had the closest agreement to the sensory results for days of quality life.

Recommendations

Based on these conclusions, it is recommended that the % polars test kit be used in actual institutional use to

test its validity as an indicator of frying medium quality life. The dielectric constant (Foodoil Sensor) can also be used to gauge changes, but the polar kit is necessary to determine actual endpoints for quality life. It is recommended that the frying media be discarded when the color card readings for the polar kits are at the 5.0 level. A further note is that care should be taken that the operators using the kits should be able to discern colors.

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